VISIT…

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Specialties

PART A
PORCELAIN BRICK

Walter Lee Sheppard, Jr.
C.C.R.M., Incorporated
Havertown, Pennsylvania

Porcelain brick are used as linings very occasionally where the need is primarily for (1) ease of cleaning, (2) product purity, (3) high wear resistance, and (4) high strength, all in combination with (5) best chemical resistance. In the dye industry, in particular, there is concern about inter-batch contamination and purity of colors. Porcelain brick are white, so that residues from earlier batches are easily visible. They have zero porosity, and the surfaces are glass smooth, so they may be easily cleaned.

The *Chemical Dictionary* defines porcelain as "ceramic wear made largely of baked clay (kaolin) coated or glazed with a fusible substance." Kaolin is defined as "(china clay; white bole; argilla; porcelain clay; white clay). A white-burning clay, which, due to its great purity, has a high fusion point and is the most refractory of all clays." It gives the composition as "mainly kaolinite (40% alumina, 55% silica) plus impurities and water."

In the manufacture of chemical and electrical porcelain, the manufacturer blends together sand, clay (a mixture of kaolin and ball clay) and spar to constitute the body of the product he will form and fire. Ball clay, as defined in the *Chemical Dictionary* as a "general term for those clays that possess good plasticity, strong bonding power, high refractories, and which burn to a white or cream-colored product. These clays are fine grained, relatively pure, hydrated aluminum silicate . . . used as bonding and plasticizing agents or chief ingredients of . . . porcelains . . ., floor and wall tile." Spar is primarily a sodium and po-

tassium silicate and is used as a flux, and to lower the firing temperature. The purer the ingredients and the higher the percentage of alumina in the mix, the higher must be the firing temperature.

Because the mix used to form the bodies that are fired to produce the products are made in this manner from naturally occurring mixed or quarried materials, the chemical analyses of the bodies varies considerably, not only from manufacturer to manufacturer, but from year to year, as the deposits of the basic materials will vary, and compositions can only be indicated in general or relative terms. What they *do* determine is the crystalline phases of the mineral content, and all analytical data is based on the identity of these phases. The only characteristic that is an absolute with porcelain brick (or tile) in comparison with other forms of fired chemical-resistant blocks is zero porosity.

As most chemists know, glass and porcelain make very satisfactory laboratory equipment, resistant to almost all harsh chemicals except hydrofluoric acid, acid fluorides, and fused alkalis. Some strong corrosives, such as hot concentrated alkalis and boiling concentrated halogen acids (other than hydrofluoric) will slowly etch or attack them, but they can still serve, even in such exposures, economically for long periods.

In selecting the particular porcelain (other than a "regular" body) for a specific service, the percentage of alumina (Al_2O_3) present is a determining factor. As the percentage of alumina increases, the hardness of the end product also increases, the softening point rises, and the firing temperature must be increased. For example, a "regular" body, with probably less than 15% alumina, up to a high strength body (38-40% alumina) will be fired at approximately 2200°-2400°F (1200°-1300°C). An 85% alumina body is fired at about 2700°-2800°F (1500°-1550°C) and a 95-98% body at 2900°-3100°F (1600°-1700°C). Hardnesses on the Mohs scale vary from 6-7 for a regular body, and 7-7.5 for a high strength body, to 9 at 98-99% alumina. Compare these figures with those for acid brick which are fired in the ranges 1900°-1950°F (1040°-1070°C) for shale, and 2100°-2200°F (1150°-1200°C) for fireclay.

Obviously, the higher the alumina content, the higher the cost of a porcelain brick lining. For example, the cost of "regular" body porcelain brick for lining a vessel will be roughly 10% of that for porcelain brick of the 85% alumina class, and except for services involving very high temperatures (which can be approximated as a percentage of the firing temperature), there will be little difference in the performance of the materials.

The following table provides a comparison of the physical properties and mineralogical composition of the "regular" body and the "high strength" body (38-40%) porcelain brick.

In manufacturing, after selecting the raw materials, and proportioning and mixing them, brick may be formed, prior to firing, either by casting or pressing. Pressing may be done in a number of ways, but whatever system is used, the end requirement is *zero* porosity. Any number of shapes are available from the manufacturers, and in a variety of thicknesses, glazed or unglazed. The reader desiring more detailed information may be referred to either *Introduction to Ceramics*, by W.D. Kingrey, M.I.T. (John Wiley and Sons), or *Ceramics: Industrial Processing and Testing*, by G.T. Jones and M.F. Berard (Iowa State University Press, Ames, Iowa).

BODY PROPERTIES

	Regular Body	High Strength Body
FIRED SPECIFIC GRAVITY	2.41	2.80
DENSITY	.087 lbs/cu.in.	.10 lbs/cu.in.
HARDNESS (Moh Scale)	6-7	7
POROSITY (Fuchsine Dye Test)	Zero at 100,000 lbs/sq.in.	Zero at 100,000 lbs/sq.in.
COMPRESSION STRENGTH	100,000 psi	140,000 psi
TENSILE STRENGTH	5,000 psi	8,000 psi
MODULUS OF RUPTURE (Unglazed)	10,500 psi	20,000 psi
MODULUS OF RUPTURE (Glazed)	15,000 psi	25,000 psi
MODULUS OF ELASTICITY	10.4×10^6 psi	17.0×10^6 psi
LINEAR THERMAL EXPANSION	3.2×10^{-6} in/in/°F	3.7×10^{-6} in/in/°F
PUNCTURE STRENGTH (3/8" Section)	400 kv/in.	----
(1/8" Section)	----	400 kv/in
DIELECTRIC CONSTANT (1 mc)	5.6	6.9
POWER FACTOR (1 mc)	0.8%	0.63%
THERMAL CONDUCTIVITY	8.4 BTU/sq.ft./in/hr/°F	approximately 10.0

COMPOSITION (Fired)

GLASS PHASE	75.0%	50.0%
MULLITE ($3Al_2O_3 \cdot 2SiO_2$)	15.0%	10.0%
QUARTZ (SiO_2)	10.0%	2.0%
ALUMINA (Al_2O_3)	---	38.0%
	100.0%	100.0%

The designer may note that if he requires the most cleanable surface, yet the least expensive lining, it is entirely feasible to mate porcelain brick as a facing with an acid brick lining, since their coefficients of thermal expansion are quite similar.

The author wishes to thank Mr. Zoltan Szilagyi, of the Lapp Insulator Company, LeRoy, NY, for his assistance in preparing the above paper.

PART B
BASALT BRICKS

Hans J. Hoffmann

Abresist Corporation
Urbana, Indiana

WHAT IS RAW BASALT?

Raw basalt deposits can be found in many parts of the world with varying external characteristics and mineralogical compositions. For example, the raw basalt deposits out of the tertiary era are subvolcanic rock and occur in the form of cylindrical plugs or bedded veins.

The cleavage face of basalt is usually column shaped. These columns stand at right angles to the cooling surface. Generally, only olivine and augite appear as phenocrysts. The base materials for these basalts are composed of plagioclase augite and magnetite; glass is relatively rare.

MANUFACTURE OF FUSED CAST BASALT

Dense, select basalt with uniform structure is required for the manufacture of fused cast basalt.

The raw basalt is mined, crushed, and melted at 2300°F (1250°C) and poured into sand or iron molds. The solidified material is placed in the annealing furnace, where temperature is raised and lowered in a specific range, for up to two days to achieve a uniform and fine crystalline structure. This gives the material its extreme hardness and resistance.

Fused cast basalt is cast in many shapes. Standard flat surfaces can be lined with square or rectangular standard flat tiles. Cylinders for pipe systems are made in static or centrifugal casting procedures. Wall thickness ranges from 21 mm for centrifugal spun cast cylinders to 30 mm thickness for the statically mold cast cylinders and tiles. Thicker liners can also be made.

CHEMICAL ANALYSIS

The average analytical composition of basalt is:

Name	Formula	Amount
Silica	SiO_2	~45-48%
Alumina	Al_2O_3	~14-16%
Iron oxides	Fe_2O_3 and FeO	~12-14%
Calcium oxide	CaO	~10-12%
Magnesium oxide	MgO	~8%
Potassium and sodium oxides	K_2O and Na_2O	~6%
Titanium oxide	TiO_2	~2%
Manganese and sulfur	Mn and S	Trace

About 45% of the iron is as magnetite compound, Fe_3O_4, and about 55% in silicates (primarily augite).

THE USE OF FUSED CAST BASALT

The manufacture of the fused cast basalt was pioneered in West Germany about 60 years ago. Fused cast basalt, also known under the registered trademark ABRESIST, is abrasion and corrosion resistant. The material is used worldwide in virtually all industries to protect equipment from the destructive forces of wear.

Typical equipment that may be lined include, but are not limited to: chutes, hoppers, flumes, conveyors, tanks, vessels, cyclones, separators, mixers, etc.

Pipe systems can be operated under a liquid head, under pressure or vacuum or under gravity conditions.

In general, it may be said that basalt linings provide long-maintenance-free service life.

PROPERTIES OF FUSED CAST BASALT

Hardness Mohs scale (diamond = 10)	About 8
Density	175 lb/ft^3
Water absorption	0% by weight
Compressive strength	71,000 lb/in^2
Bending strength	4.2 x b^3 lb/in^2
Modulus of elasticity	14-17 x 10^6 lb/in^2
Linear thermal expansion (at 200°F)	4 x 10^{-6} in/in °F
Thermal conductivity (at 200°F)	8 $Btu/in/ft^2/hr/°F$
Operating temperature limit	About 700°F
Electrical resistance (tested at 3 volts and 1 mm distance)	10,000 ohms

CHEMICAL RESISTANCE OF FUSED CAST BASALT

Fused cast basalt does not degrade and maintains a smooth surface at all times. The chemical resistance of the material is very good. Typical test results are shown on the following pages. Though chemical resistance data to many specific chemicals at specific temperatures has been determined, the user is advised to run his own tests to be certain of resistance under his own specific conditions. Varying concentrations of the chemicals and the operating temperature may result in different influences on the lining.

Choice of Setting Material

Another consideration for proper application of fused cast basalt tile under chemical attack is the proper choice of the bonding and setting material. The type of mortar required will vary depending on the exposure and the operating conditions. Setting materials may include: hydraulic mortars, silicates, resins, sulfur or mastics.

Type of Tile Construction

Plain (nonplug type) tile for installation with a mortar is recommended under chemical conditions. A membrane system may be required. Mechanically attached tile is generally not recommended under a liquid head. This holds true under chemical situations. The fluids or moisture will penetrate through a bolt or welded hole, causing attack of the base material, and resulting in premature failure of the lining. This holds true for all types of ceramic tile lining materials, be it fused cast basalt, high alumina ceramics, silicon-carbide ceramics, or any other.

RESISTANCE OF FUSED CAST BASALT TO BASES

The following tests were made to demonstrate the resistance of the fused cast basalt to various bases. The values cited are average values.

Base	Test Temperature	Resistance (%)	Test Procedure
Potash lye (25% KOH) hot, flowing	175°F	100	Operational test; no weight loss after 112 days.
Potash lye (10% KOH) stationary	70°F	100	Material Testing Institute, Neuwied, W. Germany; no weight loss after 30 days.
Soda lye (25% NaOH) hot, flowing	175°F	Almost 100*	Operational test; weight loss of 0.6% after 9 months.
Soda lye (10% NaOH)	70°F	Almost 100*	Materials Testing Institute, Neuwied, W. Germany, 0.9% weight loss after 30 days.
Soda solution (5% Na_2CO_3)	70°F	Almost 100*	Materials Testing Institute, Neuwied, W. Germany, 0.2% weight loss after 30 days.
Calcium chloride ($CaCl_2$) pasty and flowing stationary	70°F	100*	Operational test; no weight loss after 25 days.

*Plate test.

RESISTANCE OF FUSED CAST BASALT TO ACIDS

The following tests were made to demonstrate the resistance of the fused cast basalt to various acids:

Acid	Test Temperature	Resistance (%)	Test Procedure
Hydrochloric acid (25% HCl), flowing	60°F	Almost 100* Protective Layer	Operational test up to 41 days, weight loss less than 0.2%; weak bleaching of surface.
Hydrochloric acid (38% HCl), stationary	60°F	Almost 100*	Materials Testing Institute, W. Germany; 0.6% weight loss after 30 days.
Sulfuric acid (40% H_2SO_4), stationary	60°F	100	Operational test; no weight loss after 60 days.
Sulfuric acid (94% H_2SO_4), stationary	60°F	Almost 100*	Materials Testing Institute, Neuwied, W. Germany; 0.4% weight loss after 30 days.
Sulfuric acid (H_2SO_4)	60°F	Almost 100*	0.003% weight loss after 7 days (19 Dec. 1968).
Nitric acid (65% HNO_3), stationary	60°F	100*	Materials Testing Institute, Neuwied, W. Germany; no weight loss after 30 days.
Hydrofluoric acid (20% HF)	60°F	Limited resistance*	Operational test; 0.5 mm was etched away at surface after 20 days
Hydrofluoric acid (40% HF)	60°F	Limited resistance*	Materials Testing Institute, Neuwied, W. Germany; 22.8% weight loss after 30 days.
Propionic acid, stationary	60°F	100*	Materials Testing Institute, Neuwied, W. Germany; no weight loss after 30 days.
Lactic acid (8%) flowing, stationary	60°F	100	Tests by many dairies and the Kiel Testing Institute, W. Germany; no weight loss after 3 years.

*Plate test.

CONCLUSION

Fused cast basalt has an established place in the field of chemically resistant masonry. These linings will work particularly well when the chemical attack is combined with the abrasive action of sharp, hard particles. Worldwide, many in-

stallations operate under such conditions. U.S. installations include pickling lines, desulfurization vessels, etc.

Acknowledgement

Technical data was taken from the *Handbook of Abrasion and Corrosion Resistant ABRESIST Linings* by Abresist Corp., S.R. 13 North, Urbana, Indiana 46990, a subsidiary of Schmelzbasaltwerk, 5461 Kalenborn, West Germany.

PART C
CORROSION OF SILICON CARBIDE PRODUCTS

John A. Bonar

Refractories Division
Sohio Engineered Materials Co.
Niagara Falls, New York

INTRODUCTION

Silicon carbide is a man-made mineral which has high hardness, is generally chemically inert and can be obtained in the form of refractories and special components. Refractories made from silicon carbide can be obtained with a wide range of bond systems while specialized components have a few types of bond systems.

BOND SYSTEMS

Bond systems are generally the key in assessing how any refractory, including silicon carbides, will perform in contact with a corrodent. Permeable silicon carbide refractories can be classified as:

Oxide bonded (SiO_2, $Al_2O_3 \cdot SiO_2$, silicate glass)

Si_2ON_2 (silicon oxynitride)

Si_3N_4 (silicon nitride).

All of these refractories are permeable to gasses and liquids. The relatively high surface area allows the bond system to be readily attacked if it is susceptible to dissolution by the corrodent.

Several silicon carbides are available as fine grained impermeable high tolerance components. These products can be classified as:

Reaction Bonded (SiC bond with residual Si)

Sintered (either alpha or beta SiC bond with a sintering aid).

All permeable SiC refractories start with alpha silicon carbide grain which is formed by standard forming methods such as pressing, tamping, vibrating or casting into shapes with binders added in the mixing stage. After firing at elevated temperatures in either air or nitrogen, the desired final bond phase is formed.

Reaction bonded silicon carbides are formed by all of the above techniques. They are then fired in an atmosphere where large amounts of silicon metal is available to react with carbon in the compacted part to form a silicon carbide bond at high temperatures. Residual silicon is left in the pores of these products after firing.

Sintered silicon carbides are formed by all the traditional methods as well as standard plastic forming techniques such as injection molding. These compacts are sintered with small amounts of additives at very high temperatures in inert atmospheres to form essentially a single phase silicon carbide structure.

Table 19-1 details typical properties of permeable and impermeable silicon carbides.[1-4]

Table 19-1: Typical Physical Properties of Commonly Used Silicon Carbide

Property	SiO_2 Bond	Al_2O_3-SiO_2 Bond	Si_3N_4 Bond	Si_3N_4-Si_2ON_2 Bond	SiC Reaction Bond	SiC Sintered Alpha
Modulus of rupture (psi at 70°F)	3,000	3,500	6,200	6,200	47,000	80,000
Density (g/cm^3)	2.57	2.58	2.62	2.60	3.09	3.10
Porosity (%)	14	14	15	15	0.0	0.0
Thermal expansion coefficient (mean) (in/in/°F) x 10^{-6}	2.6	2.6	2.6	2.6	2.8	2.2
Thermal conductivity (Btu-in/hr/°F/ft^2)	109	109	113	113	174	170
Specific heat (mean cal/g/°C)	0.28	0.28	0.28	0.28	0.34	0.22
Permeability (cc of air/min/in^2/in in H_2O pressure)	3.5	3.2	3.0	3.8	Imp.	Imp.
Chemical analysis						
SiC	90.0	88.0	75.0	86.0	92.0	100.0
SiO_2	8.5	9.6	0.5	0.6	–	–
Al_2O_3	0.7	1.6	0.3	0.3	–	–
Si_3N_4	–	–	23.5	–	–	–
Si_2ON_2	–	–	–	13.0	–	–
Si	–	–	–	–	8.0	–

CORROSION MECHANISMS

In general, corrosion resistance is determined by the stability of the various phases present and the surface area available to attack.

Permeable refractories are thus generally more susceptible to corrosion due to their porosity and the consequent high surface area of bond phase exposed to the corrodent.[5] There are very few corrodents which would significantly attack SiC by dissolution in an aqueous medium. If SiC is attacked, the general mechanism is one of oxidation of the SiC to SiO_2. The SiO_2 is usually then removed as a reaction product exposing fresh SiC surfaces to corrosion.

ACIDIC SOLUTIONS

Attack or corrosion of the permeable silicon carbides in aqueous media is generally concerned with corrosion of the commonly used bond phases. Generally, SiO_2 bond phases are the most stable in contact with all acids except hydrofluoric. Even then, concentrations up to 200 to 400 ppm can be handled safely by silicon carbides bonded by SiO_2 for long periods of time if temperatures are generally below 200°-250°C.

Mixed oxide, Al_2O_3-SiO_2, bond phases are generally the next most corrosion resistant to acids including low quantities of HF. Silicon nitride and silicon oxynitride bonded silicon carbides perform similarly to mixed oxide bonds. Table 19-2 shows typical weight loss and retained strength values for these products in contact with common acidic solutions for the times and temperatures shown.[6]

Table 19-2: Typical Corrosion Resistance of Permeable Silicon Carbides

Bond Phase	Corrodent	Weight Change %	% Initial Strength Retained	T, °C	Time of Test, hr
SiO_2	10% NaOH	-0.6	65	96	336
Al_2O_3-SiO_2	10% NaOH	-1.0	74	96	336
Si_3N_4	10% NaOH	+0.05	96	96	336
Si_3N_4-Si_2ON_2	10% NaOH	-2.00	74	96	336
SiO_2	10% HCl	-0.6	84	96	336
Al_2O_3-SiO_2	10% HCl	-0.3	82	96	336
Si_3N_4	10% HCl	-0.4	81	96	336
Si_3N_4-Si_2ON_2	10% HCl	-0.4	91	96	336
SiO_2	10% HNO_3	0.4	85	105	336
Al_2O_3-SiO_2	10% HNO_3	-0.1	85	105	336
Si_3N_4	10% HNO_3	-0.2	78	105	336
Si_3N_4-Si_2ON_2	10% HNO_3	-0.3	99	105	336
SiO_2	40% H_2SO_4	-0.4	100	110	336
Al_2O_3-SiO_2	40% H_2SO_4	-0.2	81	110	336
Si_3N_4	40% H_2SO_4	-0.1	71	110	336
Si_3N_4-Si_2ON_2	40% H_2SO_4	+0.1	85	110	336
SiO_2	99% H_2SO_4	+0.2	74	220	100
Al_2O_3-SiO_2	99% H_2SO_4	-0.1	63	220	100
Si_3N_4	99% H_2SO_4	-0.1	74	220	100
Si_3N_4-Si_2ON_2	99% H_2SO_4	+0.3	91	220	100

(continued)

Table 19-2: (continued)

Bond Phase	Corrodent	. . 30 ppm HF . . Weight Change %	Strength Retained %	. 100 ppm HF . . Weight Change %	Strength Retained %	. . 200 ppm HF. . . Weight Change %	Strength Retained %
SiO_2	80% H_2SO_4 0.5% HNO_3	-0.3	93	-0.3	100	-0.02	91
Si_3N_4	80% H_2SO_4 0.5% HNO_3	+0.7	97	+0.6	95	+0.2	73
Si_3N_4-Si_2ON_2	80% H_2SO_4 0.5% HNO_3	+4.4	100	+2.4	85	+2.9	93

T = 150°C, t = 200 hours.
Samples were ¾" x ¾" x 4½" bars.

Impermeable silicon carbides of both types, sintered and reaction bonded, perform generally better than the permeable refractories as shown in Table 19-3.[2,6] Both reaction bonded and sintered products can be exposed to higher temperature for longer periods of time with lower weight loss than the oxide, Si_3N_4 or Si_2ON_2 bonded refractories. This is due to the lower surface area available for reaction and to the greater relative inertness of their bond phases.

Table 19:3 Typical Resistance of Impermeable Silicon Carbides Corrosion Rate (mils/yr)

Corrodent	Reaction Bonded	Sintered	T (°C)	Time of Tests (hr)
25% NaOH	73	-	Boiling	144
50% NaOH	-	2.5	100	144
10% Na_2CO_3	0.0	-	100	1,000
10% Na_2SO_4	0.2	-	100	288
20% HCl	0.1	-	Boiling	1,000
37% HCl	0.0	-	Boiling	144
70% HCl	-	0.2	100	144
30% HNO_3	0.2	-	Boiling	144
50% HNO_3	4.0	-	200	144
70% HNO_3	1.0-1.9	-	200-225	144
70% HNO_3	-	0.2	100	144
60% H_2SO_4	0.0	-	200	144
80% H_2SO_4	0.0	-	Boiling	144
95% H_2SO_4	1.2	-	225	144
95% H_2SO_4	-	1.8	100	125-300
40% H_3PO_4	0.0	-	Boiling	144
60% H_3PO_4	0.0	-	Boiling	144
85% H_3PO_4	2.3	-	Boiling	144
85% H_3PO_4	-	0.2	100	144
40% HF/10% HNO_3	100	-	60	576
10% HF/57% HNO_3	-	0.2	25	100
53% HF	-	0.2	25	100

BASIC SOLUTIONS

Silicate, Si_3N_4 and Si_2ON_2 bonded permeable refractories do not perform well in contact with sodium hydroxide. Even the reaction bonded and sintered products suffer large relative weight losses compared to their performance in acids. Sintered products do perform acceptably in this environment up to about 100°C. In general, Na_2CO_3 and NH_4OH solutions do not attack any of these refractories up to the boiling point of even high concentration solutions.

DIFFUSION REACTIONS CONTROL CORROSION

All of the reactions in acidic and basic solutions are generally controlled by diffusion of the reactant through the boundry layer existing on the exposed surfaces of the aggregate or bond phase.[5] Elevated temperatures usually increase the reaction rate. Thus, elevated temperatures and high local fluid velocities tend to increase the corrosion rate of silicon carbides as the corrosion products are swept away from the active surface sites.

CHOOSING SILICON CARBIDES FOR CORROSIVE SERVICE

When evaluating silicon carbides for potential use in corrosive service, it is preferable to look at both weight and strength changes before deciding on a material of construction. Retained strength after exposure to the operating environment developed by a laboratory screening study or from published information of actual exposures is the preferred criteria.[7] Retained strength is an excellent indicator of whether the bond phase has undergone attack and how extensive the attack may have been. This is especially important in permeable refractories where the inside of the part is exposed to the corrodent as well as the outer surfaces. Retained strength information can then be used for design purposes by imposing a safety factor on the retained strength level found from tests.

Where retained strength data is unavailable, weight loss and, if possible, volume change affects should be used as general selection criteria.

For impermeable materials such as the reaction bonded and sintered products, true corrosion rates can usually be calculated, as the reactions generally occur only on the surface of the parts.

Examination of the microstructure of the material after testing is also desirable to check for reaction deposits in pores, initiation of phase alterations not detected by weight loss measurements, or initiation of microcracking due to phase alteration reaction deposits having physical properties different from the original products.

Data should generally be for a test conducted for as long as practical but always for a minimum of 300-500 hours or more. Short time tests may mask incubation periods for attack on interior bond phases which might differ in susceptibility to corrosion as compared with the bond phases of the outer surfaces of parts, especially in Si_3N_4, Si_2ON_2 and reaction bonded products.

DESIGN

Silicon carbide brick are dimensionally stable and thus do not shrink or grow during service unless significant amounts of reaction products are present. Reaction products generally are of a lower density than the silicon carbides and may cause swelling or cracking depending on their concentration and the strength of the silicon carbide shape and the lining design.

Lining design using suitable and compatible mortars is necessary for proper performance.[8] The most superior performing lining is doomed to fail if the mortar is attacked, the mortar reacts with the brick, or the lining is not allowed to expand and contract freely during service.

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PART D
GRANITE AS CHEMICALLY RESISTANT MASONRY

Dorothy A. Richter

GEOSS
Salem, New Hampshire

INTRODUCTION

Granite is a naturally occurring, chemically resistant masonry. The silicate minerals comprising granitic rocks are not soluble in many commonly used industrial solutions and the rock has desirable physical properties such as high

strength, low permeability and low thermal expansion. Granite is a cost effective material for many industrial applications because the manufacturing process requires only the shaping of components by sawing and lapping. A further advantage is its availability in large slabs and blocks for particular industrial requirements.

DEFINITION OF GRANITE

Granite is a natural rock that crystallized from a silicate fluid within the earth's crust and consists of visibly interlocking crystals of quartz and two feldspars with lesser amounts of minerals such as micas, amphiboles or pyroxenes. The term granite as used commercially includes a much wider range of mineral compositions than the term granite used by geologists. However, most commercial granites used in applications where resistance to chemical deterioration is important are from the quartz-rich end of the range of igneous rock compositions. They may be geologically defined by such terms as granite, quartz monzonite or granodiorite. The so-called "black granites" are chemically and mineralogically very different from quartz-rich granites and are not considered here.

INDUSTRIAL USES OF GRANITE

Granite is most commonly used in applications where physical stability, durability and strength in a mildly acid environment are required. Historical uses of granite as a chemically resistant masonry include its use as flooring in places where "oil of vitriol" (sulfuric acid) was made. In the nineteenth century, granite blocks hollowed out to form tubs were employed by steel wire companies to hold dilute HCl baths for pickling off mill scale from the wire. Some of these tubs are still in use today.

There are currently three main areas of granite use in industry, although it could be used more widely.

Granite Surface Plates

Precision ground flat slabs of granite are used in a variety of industries as inspection surfaces and machine bases. Surface plates range in size from a few square inches of surface to single plates weighing 60 tons. The surfaces can be ground to tolerances of a few 100 thousandths of an inch per square foot of surface. Granite is specified for surface plates because of its stable physical properties, resistance to corrosion and abrasion, and its availability in large homogeneous slabs.

Granite Press Rolls

Cylinders of granite are used in pressing pulp webs in the manufacturing of newsprint. The granite rolls range in size from 5 feet long by 2 feet diameter to 30 feet by 6 feet. The temperature in the newsprint making machines range from

ambient to around 175°F and the pH may be as low as 5.5 from the release of sulfuric and phosphoric acids by the pulp. Granite is used to make pulp press rolls because of its resistance to deterioration under those conditions and the desirable release characteristics of the pulp web from the granite surface.

Granite Skid Caps and Tank Liners in Steel Pickling Lines

Granite is used to form tank liners (bottoms, walls and covers) and skid caps and skid bars in and between tanks in continuous acid pickling lines for the descaling of steel. The acid baths are commonly 10-15% solutions of HCl or H_2SO_4, and $FeCl_3$ or $Fe_2(SO_4)_3$ at temperatures of about 200°F.[1] The granites selected for use as skid caps and tank liners are generally quartz-rich because they are resistant to the abrasive and impact wear of the sliding steel as well as the corrosion from the acid baths.

PROPERTIES OF GRANITE

In Tables 19-4 and 19-5, the chemical and physical properties of granite masonry are given. Because the values vary greatly from granite to granite, the range in values for granite is given together with the values for Barre, Vermont gray granite, a widely used industrial granite. The ranges of values given in Table 19-5 are not absolute but are a guide to possible values for all granites. It is recommended that the properties for a particular granite be obtained and evaluated before using it as chemically resistant masonry.

Table 19-4: Chemical and Mineralogical Composition of Granites

Chemical Composition	Range for Granites[2]	Barre, VT Granite[3]
SiO_2	66.0-72.0	68.1
TiO_2	0.2-0.5	0.3
Al_2O_3	13.2-17.0	16.5
Fe_2O_3	0.2-1.5	0.3
FeO	1.2-2.7	1.3
MnO	0.0-0.1	tr
MgO	0.7-1.7	0.8
CaO	1.8-3.8	2.4
Na_2O	3.5-3.8	3.6
K_2O	2.7-6.0	5.3
H_2O	0.5-0.9	0.6
P_2O_5	0.2-0.7	tr
CO_2	0.0-1.0	0.7

Mineral Composition

Mineral Name	Chemical Composition	Range for Granites	Barre, VT Granite
Quartz	SiO_2	10-40	26.5
Microline	$KAlSi_3O_8$	15-50	15.2
Plagioclase	$NaAlSi_3O_8$-$CaAl_2Si_2O_8$	15-50	43.1
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	0-18	9.3
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	0-15	5.5
Amphibole	$(Na,Ca)_3(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH)_2$	0-25	-
Pyroxene	$(Ca,Mg,Fe)_2Si_2O_6$	0-25	-

Table 19-5: Physical Properties of Granites

	Range for Granites[4,5]	Barre, VT Granite[6]
Absorption (%)	0.1-0.4	0.23
Porosity (%)	0.4-2.0	0.5
Permeability (darcies)	Not available	10^{-6}*
Density (lb/ft^3)	157-170	165
Shore hardness	70-100	89
Compressive strength (psi)	14-47 x 10^3	28.6 x 10^3
Shear strength (psi)	3,700-4,800	4,632
Modulus of rupture (psi) average	1,430-3,060	2,484
Coef. of thermal expansion (in/in/°F)	3-5 x 10^{-6}	3.8 x 10^{-6}
Thermal conductivity (Btu/hr-ft-°F)	1-3	2

*From Reference 7.

The properties that make granite an attractive chemically resistant masonry are its naturally low permeability, thermal expansion (in generally the same range as that of "acid-brick"), high strength and the insolubility of its component minerals in dilute HCl and H_2SO_4. Hydrofluoric acid is the only acid in which quartz, feldspar and mica, the major constituents of most industrial granites, are easily soluble. Contact with HF must therefore be avoided.

Granites containing more than trace quantities of certain minerals should be avoided when selecting a granite for industrial use. Carbonate minerals such as calcite ($CaCO_3$) and siderite ($FeCO_3$) are highly soluble in HCl. Sulfide minerals such as pyrite (FeS_2) are soluble in H_2SO_4. If present in veins and crack fillings, the presence of these minerals can significantly affect the life of the industrial product.

In general, a fine grain size ($\leqslant$5 mm) is desirable in an industrial granite because it evens out the varying physical properties of the individual mineral crystals in a smaller area. There are no major chemical changes and no crystallographic phase changes in the major components of granite below 1063°F (573°C).

The physical properties of granite are generally not isotropic. The degree of anisotropy varies in different granites from almost 0 to 30%. The anisotropy of physical properties is due to the differing stress histories of granite bodies causing a preferred orientation to mineral grains and/or the microcracks in the granite. The three principal directions are called "rift," "grain" and "headgrain" in order of increasing difficulty in splitting the stone. Because the headgrain is the strongest direction, it is usually oriented in the vertical direction in surface plates and skid caps and oriented on the end of paper rolls. The values of the physical properties in Table 19-5 are perpendicular to the headgrain for those properties that are a function of specimen orientation.

GRANITE FABRICATION AND LIMITATIONS

Granites can be quarried in blocks weighing up to 100 tons. The size limitations are controlled by natural fractures in the quarry and in the lifting capacity of the quarry equipment. In most cases, however, smaller granite components are acceptable. The rough blocks are sawed and ground into the desired shape.

Granite can be finished to desired surface roughness by lapping. Precision grinding can produce surfaces flat to within 25 millionths inch per square foot surface.

Little maintenance is required of granite components other than cleaning. Worn surfaces can be reground if necessary.

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PART E
PORTLAND CEMENT/AGGREGATE BRICK

Larry C. Stephans
Rochester, New York

Portland cement exhibits good resistance to attack by some chemicals, particularly those with a basic pH. This chemical resistance allows its use in the chemical resistant masonry linings of pulp and paper mill vessels. For example, in lined kraft digesters, portland cement is used in the mortar mix for setting the carbon brick lining and in the backing grout for these linings. Kraft digesters operate under very alkaline conditions and at temperatures as high as several hundred degrees farenheit. It is also used in vessels storing concentrations of caustic as high as 40%. Because of the relatively low cost of portland cement/aggregate mixes and the corrosion resistance to media with a basic pH, it would be advantageous if this type of mix could be used for an entire lining.

The use of a portland mortar as a trowel applied lining is impractical because it will not bond to a steel substrate. A structural concrete tank is also im-

practical for containing a highly alkaline liquid because of the difficulty of building a liquid tight concrete tank and the problems that would be caused by leakage of an aggressive chemical. The problems of containing a liquid in a concrete tank are compounded if the tank is above ground and the chemicals are hot. A practical method for creating a complete lining using a portland cement mix is to make dense portland cement aggregate brick.

Portland cement brick is being manufactured and used to line some pulp and paper mill vessels. These bricks are composed of portland cement and a highly alkali resistant aggregate. The portland cement brick presently available measures 19.37 cm (7.625 inches) by 22.86 cm (9 inches) by 6.35 cm (2.5 inches). The aggregate is specially selected for its alkaline resistance and is sized to produce a brick of optimum density. The density achieved in the currently available brick is 2.2-2.3 g/cc (138-145 lb/ft^3). The compressive strength of these brick is approximately 4,220-5,625 kg/cm^2 (6,000-8,000 psi) with a cold water absorption of 4-6 weight percent.

The bricks are manufactured by combining the portland cement, aggregate, and water in carefully controlled proportions. The bricks are then pressed and cured under controlled conditions to form a portland cement brick which is excellent for lining use.

These bricks find relatively frequent use in Kraft mills because of the amount of alkaline media encountered. They are used in the liquor regeneration systems, the smelt tank, the lime slaker, the causticizer, the liquor storage tanks, and the caustic storage tanks. They, of course, can be used in any industry having corrosive alkaline conditions. As with any corrosion resistant material of construction, proper care must be exercised to insure the proper application of portland cement brick.